

## SINGLE-STAGE, SLURRY-CATALYZED CO-PROCESSING DEVELOPMENTS

John G. Gatsis, Carl L. Lea, and Mark A. Miller  
UOP Research Center  
Des Plaines, Illinois, 60017

### INTRODUCTION

UOP is currently in the sixth year of a co-processing research program sponsored by the U. S. Department of Energy (DOE). Earlier work, under completed contract DE-AC22-84PC70002, has been reported in a series of papers and reports (1-7). The overall objectives, to evaluate the technical feasibility of the co-processing concept and to establish a co-processing process data base, were met. The concept of single-stage, slurry-catalyzed co-processing was successfully demonstrated in laboratory batch experiments (1). The concept was further extended to include continuous bench-scale operations (2). Good long-term operability of the process was demonstrated in the continuous pilot plant for nearly 2,000 hours on stream (3). Typical yields and conversions from this run are shown in Table 1. A method of recovering the catalyst was developed and demonstrated on the laboratory scale. Catalyst recovery exceeded 95%. On the basis of the long-term operability and catalyst recovery studies, a conceptual commercial design was completed for a co-processing unit integrated with a 100,000 BPSD conventional refinery (3,4).

The overall objective of the current contract, DE-AC22-87PC79818, is to extend and optimize the single-stage, slurry-catalyzed co-processing scheme. Specific objectives are to improve and define catalyst utilization and costs, determine the process response to changes in resid composition and different coals, investigate the process response to changes in key operating variables, define optimum operating conditions, and reassess the economics of co-processing.

Catalyst economics play a major role in determining the overall profitability of slurry-phase co-processing. Consequently, much work has been devoted to exploring new catalyst systems and improving catalyst activity, dispersion, and recovery techniques. A new catalyst that is more active than the previous reference catalyst was identified in autoclave screening tests. This molybdenum-based catalyst is currently being evaluated in the continuous bench-scale unit. A study of the effect of catalyst concentration and increased process severity on product yields and plant operability has recently been completed and is the subject of this paper.

### EFFECTS OF CATALYST CONCENTRATION AND INCREASED PROCESS SEVERITY

#### Program Objective

The overall objective of the current work is to study the interaction of catalyst concentration and increased process severity in the continuous bench-scale unit. A specific objective is to determine the optimum conversion level required to produce high liquid yields by selective catalytic conversion as opposed to thermal conversion. This study should lead to a better understanding of how the catalyst

functions and how it can best be utilized in co-processing to accelerate reactions and decrease intrinsic activation energy. Previous experience has indicated that optimum operation is achieved at less-severe operations, where undesirable regressive recombination reactions are minimized.

#### Continuous Bench-Scale Operations

A simplified block diagram of the pilot plant is shown in Figure 1. The unit contains many of the essential features of the commercial flow scheme and is equipped to quantitatively measure the hydrogen consumption in the operations. The slurry feed (finely ground coal, petroleum vacuum resid, and catalyst) is combined with a hydrogen-rich recycle gas and is preheated before it enters the bottom of an upflow reactor. The products from the reactor are separated into gas and oil streams in the high-pressure separator (HPS). The gas stream from the HPS is combined with makeup hydrogen before being recycled back to the incoming fresh feed. A portion of the oil stream from the HPS is recycled back to the incoming fresh feed, and the remainder is sent to a stripper. The lighter hydrocarbon stream from the stripper is sent to a debutanizer, where it is separated into  $C_4$  and  $C_5+$  products. The heavier hydrocarbon stream from the stripper is sent to a vacuum fractionator to recover an overhead stream (light oil and vacuum gas oil) and a bottoms stream containing catalyst, coal minerals, insoluble carbonaceous material, and nondistillable hydrocarbons.

#### Feedstocks

The feedstocks used for this study were reference feedstocks, Lloydminster vacuum resid, designated as R10, and Illinois No. 6 coal designated as C1.4. Feed properties are given in Tables 2 and 3.

Lloydminster vacuum resid (950°F<sup>+</sup>, 120-150 Pen.) was obtained from a commercial refinery in Canada.

Illinois Coal No. 6 was obtained by the Kentucky Center for Energy Research Laboratory from the Burning Star Mine. Grinding (thru 200 mesh) and drying were done by Empire Coke Company of Holt, Alabama. The preparation procedure and equipment have been previously described (5).

#### Process Conditions

For each given catalyst concentration, a temperature survey was conducted with a 2:1 mixture of resid to coal, at 3000 psig and base WHSV. The reactor temperature was increased in a stepwise manner from 420°C until evidence of thermal degradation or reactor fouling was observed. Heptane insoluble conversion, which is primarily controlled by catalytic effects, was monitored to determine the process response to temperature. Three catalyst concentrations, 0.50, 0.12 and 0.05 wt-% Mo, were studied.

#### 0.50 wt-% Mo Catalyst Temperature Study

The first study was made with 0.50 wt-% molybdenum (Mo) catalyst, measured on a metal per moisture and ash free feed (MAFF) basis. The run was started at 422°C, and the temperature was increased in a

stepwise manner. Six test conditions (422, 427, 440, 451, 457, and 467°C) were run. The plant operated well, even at the higher processing temperatures and showed no evidence of either thermal degradation or reactor fouling. Surprisingly, the conversions showed a steady increase with temperature, with no sign of decrease even at 467°C. The unconverted coal (toluene insolubles less ash) did not show the characteristic increase that is typically observed as a result of coking at higher temperatures (Figure 2). Heptane insoluble conversion also showed a steady increase with temperature (Figure 3). Previous studies showed a rapid decline in heptane insoluble conversions at temperatures greater than about 430°C and coking and plugging problems limiting plant operability above about 435°C (2). The decline in conversions and increase in coking with increased temperature may be attributed to retrograde reactions in which asphaltenes in the petroleum feedstock and those formed by thermal breakup of the coal polymerize and eventually form coke. In the presence of an effective hydrogenation catalyst and hydrogen, these reactive intermediates may be preferentially converted to stable lower-molecular-weight products. However, at high temperatures, the rates of the retrogressive thermal reactions possibly exceed those of the beneficial catalytic reactions, and pitch and coke are formed at the expense of the more-desirable lighter liquid products.

Two major differences between this study and the earlier temperature studies were observed, and these differences may account for the improved high-temperature conversions and plant stability. The catalyst was changed from a catalyst based on vanadium (V) to a more-active Mo-based catalyst, and a liquid recycle stream from the bottom of the HPS to the reactor inlet was included. Space velocity was maintained constant in each study, but the addition of the liquid recycle stream (5:1 recycle to fresh feed) resulted in greater mixing and higher velocity through the reactor. The improved high-temperature conversions and plant stability may be due to better contacting of the reactive fragments with hydrogen and catalyst (as a result of increased reactor backmixing), or to the decreased relative contact between the coke precursors and the hot reactor walls due to greater superficial liquid velocities in the reactor. Hydrodynamic differences from the recycle may have also affected the flow regime, heat transfer characteristics, or gas void fraction in the reactor. How much of the improved high-temperature conversion and operability is due to the catalyst and how much is due to improved hydrodynamics resulting from use of liquid recycle is not known at this time. Further reactor modeling studies are required to thoroughly understand these phenomena.

The greatest impact of the higher temperature was the 40 wt-% increase in nondistillable conversion (Figure 4), without significant carbon loss to retrograde reactions, and only about 6% increase in light-ends yields (Figure 5). Table 4 compares the yields and product properties at 427, 451, and 467°C. The product distribution gives the expected trends with increasing temperature: an increase of lighter fractions (C<sub>1</sub>-C<sub>4</sub>, C<sub>5</sub>-177°C, and 177-343°C) and a decrease of heavier fractions (343-510°C and 510°C+). The quality of the liquid product improved with increasing temperature. The API gravity and hydrogen content of the product increased, and heptane insolubles, sulfur, and nitrogen levels decreased.

#### 0.12 wt-% Mo Catalyst Temperature Study

This run was started at 427°C, and as in the previous run, the temperature was increased in a stepwise manner. Six test conditions (427, 432, 438, 446, 451, and 459°C) were run. Plant operations were again reasonably good, and there was no evidence of thermal degradation or reactor fouling. As in the prior run, all of the conversions continued to increase with temperature over the range studied. The unconverted coal showed a steady decrease with temperature (Figure 6), and the heptane-insoluble conversion increased with temperature (Figure 7). The yields and product properties at 427, 446, and 459°C are compared in Table 5. The yields of lighter fractions ( $C_1$ - $C_4$ ,  $C_5$ -177°C, and 177-343°C) increased and the heavier fractions (343-510°C and 510°C+) decreased with increasing temperature. The increases in nondistillable conversion (Figure 8), and light-ends yields (Figure 9) were comparable to the 0.50% Mo case. The quality of the liquid product improved with increasing temperature. The API and hydrogen content increased, and heptane insolubles, sulfur, and nitrogen levels decreased, though to a lesser extent than in the 0.50% Mo case.

#### 0.05 wt-% Mo Catalyst Temperature Study

The third temperature study was conducted with a 0.05 wt-% Mo catalyst concentration. The objective of this run was to determine the low-concentration and high-temperature operability limits of the plant. Four test conditions (428, 447, 456, and 462°C) were run. Even with this low catalyst concentration, the plant operations were reasonably good, and there was no evidence of either thermal degradation or reactor fouling over the temperature range studied. As in the previous runs, all of the conversions continued to increase with temperature, and the yields and product properties follow similar trends. The yield of unconverted MAF coal, heptane insolubles, and nondistillable conversions and light-ends yield versus temperature are shown in Figures 10-13. Yields and product properties at 428, 447, and 462°C are compared in Table 6.

#### Effect Of Catalyst Concentration

An understanding of the effect of catalyst concentration at increased process severity is important to the co-processing concept. Increased conversion of petroleum resid and coal to lighter products can be achieved by increasing process severity. However, at these high conversion levels, increased hydrogen consumption and the nonselective production of light ends also occur. Degradation reactions and the fouling and coking tendency of the resid-coal mixture also tend to increase at high-severity conditions. At very high severities, thermal effects greatly predominate over catalytic effects and further accelerate the problems associated with yield loss, product stability, and coking. A wide range of nondistillable conversion levels can be achieved, merely by increasing the reactor temperature. The more-difficult task and an important part of UOP's program is to determine the optimum conversion level that produces high liquid yields by selective catalytic conversion, as opposed to thermal conversion, and reduces the problems associated with high severity operation.

Nondistillable conversion, which increased with increasing

temperature, was about the same for the different catalyst concentrations over the entire temperature range investigated (Figure 16). This result indicates that nondistillable conversion is primarily controlled by thermal effects and is not catalytically induced. Coal conversion (Figure 14) and heptane insoluble conversion (Figure 15) were more responsive to catalyst concentration, indicating that catalyst plays a role in coal and heptane-insoluble conversion. The 0.05 wt-% Mo catalyst gave slightly higher heptane insoluble conversion (Figure 15) than the 0.12 wt-% Mo. The liquid product properties were also equal to or better than the properties of the 0.12 wt-% Mo catalyst. This can be accounted for by improved catalyst dispersion for the 0.05 wt-% Mo catalyst. The effect of catalyst concentration was more pronounced at temperatures below about 440°C. At the higher temperatures, the effect of catalyst concentration diminishes, and virtually identical performance is obtained irrespective of catalyst concentration. The fact that the effect of catalyst concentration was more pronounced at the low temperature and its effect diminished at the high temperature indicates that hydrogenation, which is catalytically induced and is favored at low temperature, is being promoted by the catalyst. The catalyst provides hydrogen in an active form for stabilization of the coal-derived free radicals at the onset of coal dissolution and for the conversion of asphaltenes to thermally stable oil-soluble products. Thus, the catalyst beneficially effects the ultimate conversion and product distribution. The liquid-product properties (Tables 4, 5, and 6) followed the same trends as the coal and heptane-insoluble conversions; i.e., they improved with higher catalyst concentration, and the improvement diminished with increasing temperature. Increases in API, hydrogen content, conversion of asphaltenes, and removal of heteroatoms are primarily controlled by catalytic effects that predominate at the lower temperatures.

Two questions may be asked: what is the role of the catalyst at the higher temperature, and is it indeed needed? To answer these questions, UOP has planned a run with no catalyst. This run will provide a baseline for determining whether improved high temperature operability was due solely to improved hydrodynamics resulting from the use of liquid recycle, or whether the catalyst also plays an important role, even at very low concentrations.

#### CONCLUSIONS

The beneficial effects of increased catalyst concentration were more pronounced at lower temperatures (below about 440°C). The advantage of high catalyst concentration diminished at higher temperatures, where thermal effects dominate over catalytic effects. High nondistillable conversions, without excessive carbon loss to retrograde reactions and light-ends yields, were demonstrated. The improved operability of co-processing at high temperatures represents an important advance that may significantly improve the process economics.

## REFERENCES

- (1) J. G. Gatsis, et. al., "Coal Liquefaction Co-Processing," Proceedings of DOE Direct Liquefaction Contractors' Review Meeting, Nov. 19-21, 1985.
- (2) J. G. Gatsis, et. al., "Continuous Bench-Scale Single-Stage Slurry Catalyzed Co-Processing," Proceedings of DOE Direct Liquefaction Contractors' Review Meeting, Oct. 20-22, 1986.
- (3) J. G. Gatsis, et. al., "Continuous Bench-Scale Single-Stage Slurry Catalyzed Co-Processing," Proceedings of DOE Direct Liquefaction Contractors' Review Meeting, Oct. 6-8, 1987.
- (4) D. A. Nafis, et. al., "Bench-Scale Co-Processing," Proceedings of DOE Direct Liquefaction Contractors' Review Meeting, Oct. 4-6, 1988.
- (5) C. P. Luebke, et. al., "Coal Liquefaction Co-Processing Topical Report Number 1," Prepared for the United States Department of Energy under Contract No. DE-AC22-84PC70002, June 1, 1987.
- (6) J. G. Gatsis, et. al., "Coal Liquefaction Co-Processing Topical Report Number 2," Prepared for the United States Department of Energy under Contract No. DE-AC22-84PC70002, Aug. 19, 1988.
- (7) D. A. Nafis, et. al., "Coal Liquefaction Co-Processing Final Report," Prepared for the United States Department of Energy Under Contract No. DE-AC22-84PC70002.
- (8) D. A. Nafis, et. al., "UOP Co-Processing Developments," Proceedings of DOE Direct Liquefaction Contractors' Review Meeting, Oct. 2-4, 1989.

Table 1

### Run 19 Long-Term Operability Study

<u>Conditions:</u>	<u>Yields, wt-% MAF Coal and Resid</u>
Coal: Ill. No. 6 (C1.2)	H <sub>2</sub> S 2.2
Resid: Lloydminster Vacuum Resid (R8)	NH <sub>3</sub> 0.4
Catalyst: 1.0 wt-% V (K1.0)	H <sub>2</sub> O 5.0
Resid-Coal: 2:1	C <sub>2</sub> -C <sub>4</sub> 2.7
Temperature: 425°C	C <sub>5</sub> -371°C 28.5
Pressure: 3,000 psig	371-510°C 26.3
	510+°C 33.7
	Unc. MAF Coal <sup>a</sup> 3.7
	H <sub>2</sub> Consumption (2.5)
	100.0
<u>Conversions, wt-%</u>	
MAF Coal	89.3
Heptane Insolubles	79.5
510+°C Nondist.	56.8
371+°C Nondist.	35.7

**Table 2**  
**Petroleum Resid Analysis**

<u>Resid</u>	<u>Lloydminster Vacuum Resid (R10)</u>
API Gravity	6.6
Specific Gravity	1.0246
Distillation, °C	
IBP, vol-%	379
5	455
10	473
20	509
EP	512
Vol-% over at EP	22.0
Analysis, wt-%	
Carbon	83.6
Hydrogen	10.3
Sulfur	4.77
Nitrogen	0.59
Heptane Insolubles	13.56
Carbon Residue (MCRT)	17.39

**Table 3**  
**Coal Analysis**

<u>Coal</u>	<u>Illinois No. 6 (C1.4)</u>
Proximate Analysis	
(AR Basis), wt-%	
Volatile Matter	38.84
Fixed Carbon (1)	45.80
Moisture	4.08
Ash	11.28
Ultimate Analysis	
(AR Basis), wt-%	
Carbon	66.75
Hydrogen (2)	4.66
Sulfur	2.91
Nitrogen	1.34
Oxygen (1)	8.98
Ash	11.28
Moisture	4.08

- (1) By difference  
(2) Corrected for moisture

**Table 4**  
**Effect of Severity on Yields and Product Properties**  
**0.50 wt-% Mo Catalyst**

Temperature, °C	427	451	467
Yields, wt-% MAFF			
H <sub>2</sub> O + CO <sub>x</sub>	2.20	4.22	6.11
H <sub>2</sub> S	2.26	3.11	3.11
NH <sub>3</sub>	0.21	0.63	0.22
C <sub>1</sub> -C <sub>4</sub> (Light Ends)	2.33	6.75	8.91
C <sub>5</sub> -177°C (Naphtha)	5.90	17.17	25.46
171-343°C (Distillate)	17.61	31.54	32.59
343-510°C (VGO)	26.52	22.12	15.90
510°C+ (Resid)	40.82	15.27	8.37
Unc. MAF Coal	4.51	2.87	2.95
H <sub>2</sub> Consumption	(2.37)	(3.66)	(3.61)
TOTAL	100.00	100.00	100.00
C <sub>5</sub> + Total Liquid Product			
MAFF, wt-%	90.85	86.10	82.32
API Gravity	13.3	24.4	28.6
Carbon, wt-%	86.36	86.99	85.76
Hydrogen, wt-%	10.38	11.04	11.23
Sulfur, wt-%	1.66	0.61	0.47
Nitrogen, wt-%	0.79	0.57	0.84
Heptane Insolubles, wt-%	8.64	4.61	3.38
MCRT, wt-%	12.84	7.36	6.36



Table 5  
Effect of Severity on Yields and Product Properties

0.12 wt-% Mo Catalyst

Temperature, °C	427	446	459
Yields, wt-% MAFF			
H <sub>2</sub> O + CO <sub>x</sub>	6.7	4.0	4.3
H <sub>2</sub> S	1.6	3.3	3.5
NH <sub>3</sub>	0.2	0.4	0.8
C <sub>1</sub> -C <sub>4</sub> (Light Ends)	2.5	5.5	9.1
C <sub>5</sub> -177°C (Naphtha)	5.4	12.0	14.5
177-343°C (Distillate)	17.6	24.0	36.0
343-510°C (VGO)	29.2	26.1	22.9
510+°C (Resid)	34.0	24.2	10.3
Unc. MAF Coal	5.6	3.6	2.3
H <sub>2</sub> Consumption	<u>(2.8)</u>	<u>(2.9)</u>	<u>(3.6)</u>
TOTAL	100.0	100.0	100.0
C <sub>5</sub> + Total Liquid Product			
MAFF, wt-%	86.2	86.3	83.7
API Gravity	12.9	17.0	19.9
Carbon, wt-%	84.7	84.0	84.4
Hydrogen, wt-%	10.0	10.3	11.0
Sulfur, wt-%	2.1	1.4	1.1
Nitrogen, wt-%	0.9	0.8	0.4
Heptane Insolubles, wt-%	9.8	9.1	3.1
MCRT, wt-%	12.7	11.2	6.2

Table 6

Effect of Severity on Yields and Product Properties

0.05 wt-% Mo Catalyst

Temperature, °C	428	447	462
Yields, wt-% MAFF			
H <sub>2</sub> O + CO <sub>x</sub>	1.67	2.00	3.64
H <sub>2</sub> S	2.51	3.28	3.64
NH <sub>3</sub>	0.34	0.49	0.42
C <sub>1</sub> -C <sub>4</sub> (Light Ends)	2.75	5.68	9.10
C <sub>5</sub> -177°C (Naphtha)	5.69	13.69	23.43
173-343°C (Distillate)	11.04	25.65	27.92
343-510°C (VGO)	30.65	24.47	17.92
510°C+ (Resid)	40.66	24.03	14.66
Unc. MAF Coal	6.76	3.67	2.62
H <sub>2</sub> Consumption	(2.07)	(2.96)	(3.35)
TOTAL	100.00	100.00	100.00
C <sub>5</sub> + Total Liquid Product			
MAFF, wt-%	88.04	87.84	83.93
API Gravity	11.4	18.7	25.4
Carbon, wt-%	84.4	84.8	85.0
Hydrogen, wt-%	10.4	10.9	11.3
Sulfur, wt-%	2.4	1.5	0.9
Nitrogen, wt-%	0.7	0.7	0.7
Heptane Insolubles, wt-%	7.0	5.6	3.1
MCRT, wt-%	13.5	10.6	8.7

**FIGURE 1**

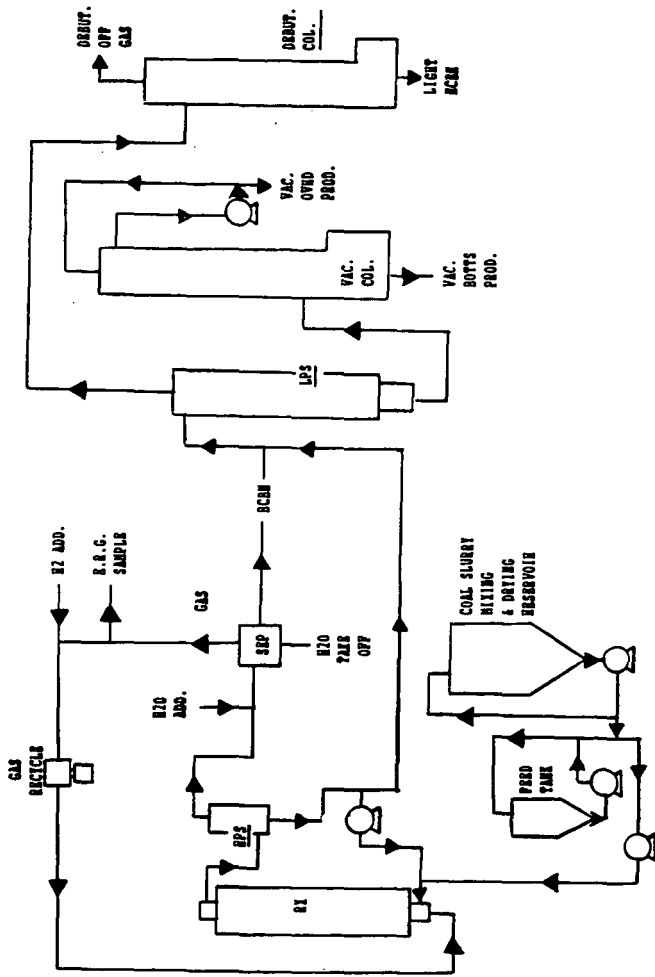


Figure 2  
Unconverted Coal Yield  
vs. Temperature

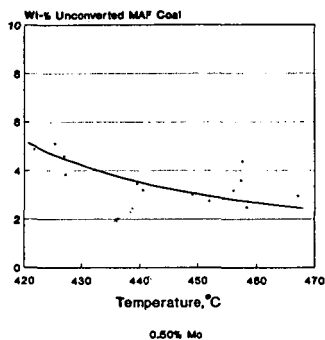


Figure 3  
Hept. Insol. Conversion  
vs. Temperature

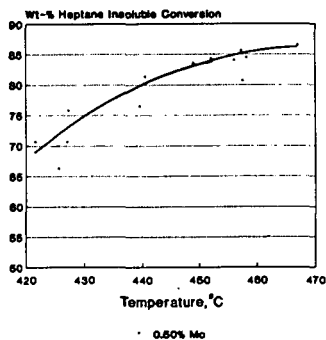


Figure 4  
Nondistillable Conversion  
vs. Temperature

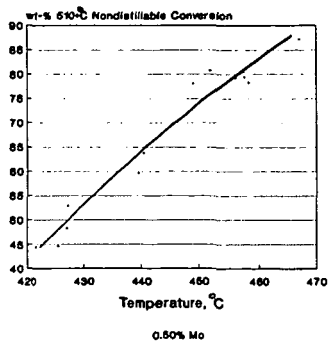


Figure 5  
Light Ends Yields  
vs. Temperature

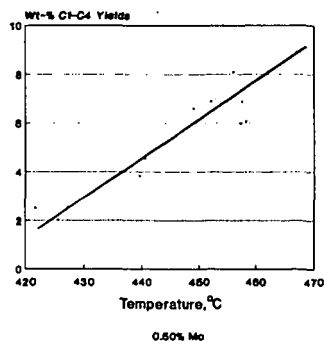


Figure 6

### Unconverted Coal Yield vs. Temperature

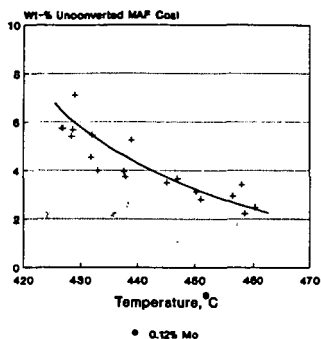


Figure 7

### Hept. Insol. Conversion vs. Temperature

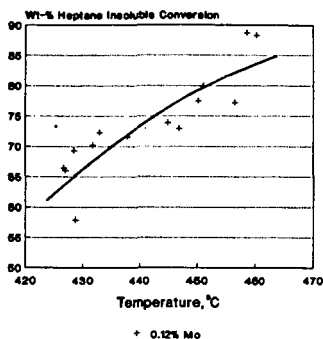


Figure 8

### Nondistillable Conversion vs. Temperature

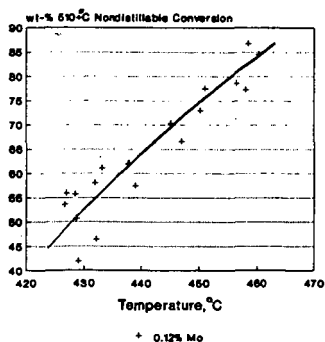


Figure 9

### Light Ends Yields vs. Temperature

